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The Osmotic Pressure of Glucose Solutions
and the
Freezing Point Depressions and Densities
# of Solutions of Glucose and Cane Sugar;
also
Some Experiments on the Osmotic
Pressure of Urea Solutions.

DISSERTATION.

Submitted to the Board of University Studies of
the Johns Hopkins University
in conformity with the requirements for the degree
of Doctor of Philosophy.

B. SMITH HOPKINS.

BALTIMORE.

1906.

12780

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PART 1

OSMOTIC PRESSURE.

THE CELL

The porouscells used in this work were prepared according to the method developed by Morse and Frazer,(1) there being no important departure from their method either in the preparation of the clay or in the grinding of the cell. Fig 1 shows the cell, the manometer and the connecting parts. The upper portion of the cell A is ground internally by a rapidly revolving carborundum disk, the grinding being continued until there is formed a well defined shoulder which acts as a support for the soapstone ring b. Two grooves, one of which is marked a in the cut, are ground in the wall of the cell to prevent the cement from being dislodged under pressure. The soapstone ring, b, is turned upon the lathe until it justslips into position against the shoulder. It must also fit exactly upon the glass tube B which serves to join the cell to the manometer C. The tube B is enlarged at c and d in order that it may not be displaced by pressure. It is constricted at c so that it may hold the rubber stopper K more securely, and it is firmly cemented to the cell as well as to the brass piece O. The brass

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(1) Am. Chem. Jour.34 1

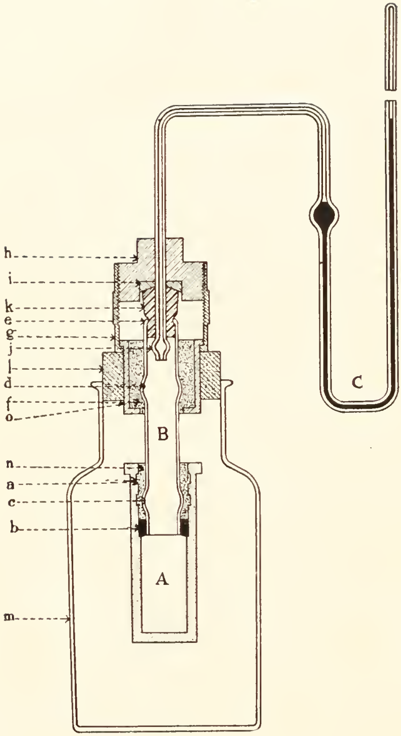

Fig. I.

collar g is so arranged that it may be slipped over the cell from beneath. It is provided with an internal flange which catches the external flange upon o and its inner surface is threaded to fit the nut h. The small brass piece i rests against the rubber stopper and its concave surface serves to hold the stopper more firmly in place. The cell is immersed in water contained in the bottle m and is held in place by the cork l.

In order to form a tight joint between the tube B and the soapstone ring, the latter is placed in position upon the former and any space which exists between them is filled with molten shellac. This is accomplished by placing the tube and ring, in an inverted position, in an air bath, covering the end with powdered shellac and heating for some hours at 110°. This treatment causes the volatile portions of the shellac to distill off. Then the outer surface of the ring and the inner wall of the cell, down to the shoulder, are painted repeatedly with a solution of rubber in carbon disulphide. After the tube and ring have been forced into position against the shoulder, the ring is covered with a quantity of the rubber solution which is afterwards heated to a temperature of 100° until it has become hard. Then a quantity of powdered shellac is poured in upon the rubber coating and the heating is repeated. In this way the joints are made tight.

The cement with which the tube B is fastened to the cell and to the brass piece o is made by mixing litharge and glycerine. The litharge is prepared by heating lead carbonate. A cement of sufficient hardness and greater durability is obtained if ten per cent of water is added to the glycerine. If the solution in the cell comes in contact with the cement, the latter is quickly disintegrated, consequently it is essential to protect the cement as described in the preceeding paragraph.

After the parts of the cell are securely cemented together and carefully dried, the air contained in the porous wall is displaced by the electrical endosmose method(1). After the removal of the air from the cell wall, the cell is kept in freshly boiled distilled water. The membrane used in this work was copper ferrocyanide,deposited electrolytically(2). When the membrane has developed a suitable resistancethe cell is ready for the measurement of pressure.

IMPROVEMENTS IN THE MANOMETER.

Several modifications of the manometer have been used. The enlargement at the lower end, shown at j Fig.1. was formerly made by enlarging the bore of the tube making a small bulb at this place. This arrangement gave considerable difficulty for reasons

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(1) Am. Chem. Jour. 34 14.
(2) Ibid 34 15.

which will appear when the taking down of a cell after a measurement is under discussion. The manometer is much more satisfactory if the enlargement at j is made by thickening the walls of the tube without enlarging its bore.

Another improvement which is not shown in Fig.1 but may be seen in Fig. 4 is a second bulb blown in the upright portion of the manometer. This additional bulb besides increasing the amount of mercury held by the manometer, makes it possible to apply diminished pressure to the manometer without danger of the enclosed air escaping around the turn C (Fig.1.) The value of this change becomes evident when the cell is being put together for a measurement, or is being taken down after the completion of an experiment.

A third change in the form of the manometer is the introduction of a short thread of mercury at the top of the longer arm, shown in Fig.4. In the form previously used the air column extended to the top of the manometer, which made the volume of the enclosed air a matter of considerable doubt(1) arising principally from two considerations: First, in closing the manometer it was necessary to soften the glass for some distance from the end, thereby rendering the calibration of this portion of the tube inaccurate, and, second, the end of the bore was never perfectly conical as it was assumed to be.

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(1) Am. Chem. Jour. 14 10.

It will be seen that both of these errors affect the upper portion of the manometer where the greatest accuracy is desired especially in the measurement of higher pressures. When the manometer is closed by the method previously used there is always more or less contamination of the air column by the carbon dioxide and moisture of the atmosphere. By introducing a thread of mercury at the top of the air column, all of these difficulties are avoided. The method used for introducing the thread will be explained later.

CALIBRATION OF THE MANOMETER.

Before a manometer can be used to measure pressures it must, of course, be carefully calibrated(1) and a curve drawn showing the corrections which must be applied to any reading on account of the inequalities in the bore of the tube. In the tables below are the calibration data for manometers No.9 and No.11. In column 1 the numbers are the actual readings obtained; column 11 showns the distance from zero, which is a mark just above the bulb on the main limb of the manometer; 111 shows the space occupied by the calibrating thread in its various positions; 1V contains the multiples of the average space filled by the calibrating thread; and column V is the correction to be applied at the several points which are established by the positions occupied

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(1) Am. Chem. Jour. 34 6.

by the calibrating thread.

TABLE 1

MANOMETER NO. 9

	1	11	111	1V	V
No.	Readings	Distance from Zero	Length of thread	Multiples of mean space	Correction values
1	904.14				
2	888.18	15.96	15.96	15.911	-0.049
3	872.20	31.94	15.98	31.822	-0.118
4	856.27	47.87	15.93	47.733	-0.137
5	840.38	63.76	15.89	63.644	-0.116
6	824.50	79.64	15.88	79.555	-0.085
7	808.60	95.54	15.90	95.466	-0.074
8	792.71	111.43	15.89	111.377	-0.053
9	776.82	127.32	15.89	127.288	-0.032
10	760.97	143.17	15.85	143.199	+0.029
11	745.12	159.02	15.85	159.110	+0.090
12	729.34	174.80	15.78	175.021	+0.221
13	713.50	190.64	15.84	190.932	+0.292
14	697.69	206.45	15.81	206.843	+0.393
15	681.85	222.29	15.84	222.754	+0.464
16	666.00	238.14	15.85	238.665	+0.525
17	650.20	253.94	15.80	254.576	+0.636
18	634.41	269.73	15.79	270.487	+0.757
19	618.59	285.55	15.82	286.398	+0.848
20	602.74	301.40	15.85	302.309	+0.909
21	586.86	317.28	15.88	318.220	+0.940
22	570.94	333.20	15.92	334.131	+0.931
23	555.02	349.12	15.92	350.042	+0.922
24	539.13	365.01	15.89	365.953	+0.943
25	523.21	380.93	15.92	381.864	+0.934
26	507.28	396.86	15.93	397.775	+0.915
27	491.29	412.85	15.99	413.686	+0.836
28	475.22	428.92	16.07	429.597	+0.677
29	459.15	444.99	16.07	445.508	+0.518
30	443.10	461.04	16.05	461.419	+0.379
31	427.04	477.10	16.06	477.330	+0.230
32	411.00	493.14	16.04	493.241	+0.101
33	394.98	509.16	16.02	509.152	-0.008

TABLE 11

MANOMETER NO.11

	1	11	111	1V	V
No.	Reading	Distance from Zero	Length of Thread	Multiples of mean space	Correction Values
1	911.50				
2	898.31	13.19	13.19	13.0918	-0.098
3	885.13	26.37	13.18	26.183	-0.187
4	871.96	39.54	13.17	39.275	-0.265
5	858.84	52.66	13.12	52.367	-0.293
6	845.70	65.80	13.14	65.459	-0.341
7	832.52	78.98	13.18	78.550	-0.430
8	819.30	92.20	13.22	92.642	-0.558
9	806.05	105.45	13.25	104.734	-0.716
10	792.86	118.64	13.19	117.826	-0.814
11	779.66	131.84	13.20	130.918	-0.922
12	766.45	145.05	13.21	144.009	-1.041
13	753.19	158.31	13.26	157.101	-1.209
14	739.99	171.51	13.20	170.193	-1.317
15	726.79	184.71	13.20	183.285	-1.425
16	713.60	197.90	13.19	196.377	-1.523
17	700.44	211.06	13.16	209.468	-1.592
18	687.25	224.25	13.19	222.560	-1.690
19	674.09	237.41	13.16	235.652	-1.758
20	660.94	250.56	13.15	248.744	-1.816
21	647.78	263.72	13.16	261.836	-1.884
22	534.68	276.82	13.10	274.927	-1.893
23	621.53	289.97	13.15	288.019	-1.951
24	608.41	303.09	13.12	301.111	-1.979
25	595.26	316.24	13.15	314.203	-2.037
26	582.16	329.34	13.10	327.295	-2.045
27	569.14	342.36	13.02	340.386	-1.974
28	556.08	355.42	13.06	353.478	-1.942
29	543.06	368.44	13.02	366.570	-1.870
30	530.07	381.43	12.99	379.662	-1.768
31	517.06	394.44	13.01	392.754	-1.686
32	504.07	407.43	12.99	405.845	-1.585
33	491.12	420.38	12.95	418.937	-1.443
34	478.19	433.31	12.93	432.029	-1.281
35	465.30	446.20	12.89	445.121	-1.079
36	452.42	459.08	12.88	458.213	-0.867
37	439.52	471.98	12.90	471.304	-0.676
38	426.61	484.89	12.91	484.396	-0.494
39	413.77	497.73	12.84	497.488	-0.242
40	400.92	510.58	12.85	510.580	-0.000

FILLING AND SEALING THE MANOMETER.

After the manometer is calibrated it is first filled with pure mercury, then the air column is introduced in the following manner. The top of the manometer is connected by a short rubber tube with a drying apparatus which is arranged to remove carbon dioxide, ammonia, and water. A three-way stop-cork is placed between the manometer and the drying apparatus. Air is repeatedly drawn into the manometer through the drying apparatus and expelled into the open air by lowering and raising a reservoir of mercury which is attached to the lower end of the manometer by a long rubber tube. When it is certain that the air which is being drawn into the manometer is sufficiently pure, a small globule of mercury is detached from the main column by pressing the rubber tube at the top of the manometer. An amount of air is then admitted which is sufficient at atmospheric pressure to reach from the top of the manometer nearly to the bulb, then the pressure is released from the tube above and the thread of mercury is drawn in. If it is too long the reservoir is lowered till all the air is drawn down into the bulb and some of the mercury is allowed to drip across the air space, joining the main quantity of mercury. When a thread about 15 millimeters in length is obtained, it should be raised nearly to the top of the manometer

to be sure that the right amount of air has been enclosed. It is, of course, desirable to enclose as large a volume of air as possible thereby making more accurate the readings in the case of higher pressures. But, on the other hand, the introduction of too much air makes it more difficult to determine its exact volume. It is generally best to have the air column of such length that, at atmospheric pressure, it reached from the top of the manometer to a point between the lower scratch and the bulb. When the right amount of air is secured, the drying apparatus is detached and the manometer is sealed. This is accomplished by sealing on a short piece of tubing and drawing out the end of the manometer to an exceedingly fine capillary, the end being left open to the air. The reservoir of mercury is now raised sufficiently to drive the thread up into the capillary nearly, but not quite, to the end. With the mercury in this position the end of the capillary is sealed; then the reservoir is lowered to give diminished pressure and heat is applied, gently at first, to the point where the capillary joins the main portion of the manometer. The heat vaporizes some of the mercury in the thread and, under the diminished pressure, the lower part of the thread moves downward. The heat is now increased, the tube is sealed and very carefully annealed. When the top of

the manometer has cooled to room temperature, the mercury thread should entirely fill its upper end.

DETERMINATION OF THE AIR VOLUME.

From the calibration data, the diameter of the main arm of the manometer at the zero point is calculated and another tube of the same diameter is selected for use as a reservoir in determining the volume of the enclosed air. This tube is joined to the lower end of the manometer by a piece of rubber tubing from which the air has been displaced by mercury. The manometer and side tube are fixed in vertical position and the amount of inclosed air is determined under slightly different pressures. As an example of the method employed, the data for manometer No.9 have been tabulated:

FOLD OUT

After the volume of air has been determined as illustrated, the manometer is ready for use.

SETTING UP A CELL

When it is desired to set up a cell for the measurement of osmotic pressure, the cell is first treated to the membrane forming process, until the resistance has reached a maximum. The cell is then washed out with distilled water rinsed and filled with the solution whose osmotic pressure is to be determined. During the setting up process the cell was formerly wrapped in absorbent material, but it was found that some of the solution was drawn out of the cell wall, air taking its place. As a result, when the cell was immersed in water, bubbles of air collected on its surface. In order to avoid this, the cell is wrapped in a wet piece of sheet rubber, or surrounded by a tube such as is used with a Gooch filter. The manometer carrying the rubber stopper K (Fig 1) is then forced into the tube B. This process requires to cooperation of two persons. One operator holds the cell firmly with one hand and with the other supports the manometer in such a manner that the nut **h** is raised to some distance above its usual position. The duty of the second operator consists in aiding the escape of the surplus solution from the cell. This is accomplished by means of an

implement known as a "fang" from its shape. It is made from the soft end of a round file in which a longitudinal groove has been cut. The end is curved somewhat in order that it may the more easily be inserted between the stopper and the tube. When the rubber stopper is being forced into position, the fang is inserted alongside. and as the pressure from without is increased some of the solution escapes from the cell. Care must be exercised not to release the pressure from the stopper while the fang is in position since if the pressure is decreased air rushes into the cell. The greatest danger of allowing air to enter the cell is at the moment when the fang is withdrawn. When the stopper is forced well into place, it is securely wound with waxed shoemakers' thread and then wrapped with insulation tape for the purpose of preventing its displacement or distortion while under pressure. Then the brass collar g is brought up over the cell and screwed into the nut h, until a rise in the mercury in the manometer shows that the sell is tightly closed. In the more concentrated solutions the nut is tightened from time to time in order to hold the stopper as rigidly as possible. Care must be exercised not to exert in this way a pressure greater than the osmotic pressure of the solution in the cell. In spite of all devices used to hold the stopper rigidly in position, in the

more concentrated solutions there has always been an upward displacement of the manometer caused either by the manometer slipping through the stopper or by a rise in the stopper itself.

The presence of the second bulb, on the main limb of the manometer, makes the operation of setting up a cell considerably easier. With the old form of manometer, which contained a single bulb, it was necessary to exert a continuous pressure upon the stopper from the time the manometer was first placed in the tube until the cell was closed and the nut tightened. For if the pressure was allowed to diminish, the enclosed air column would expand and part of the air would escape around the turn C. This made it necessary to open the manometer, refill with air, seal and redetermine the air volume. No difficulties of this nature are encountered in the new form of manometer.

CONSTANT TEMPERATURE
BATH

In order to secure satisfactory determinations of osmotic pressure it is of the greatest importance that the whole apparatus be kept at a uniform temperature throughout the experiment or at least that only slight changes in temperature shall take place and that these changes shall be very gradual. The arrangements previously described(1) for equalizing temperature have not been wholly satisfactory since the daily range of

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(1) Am. Chem. Jour. 34 22.

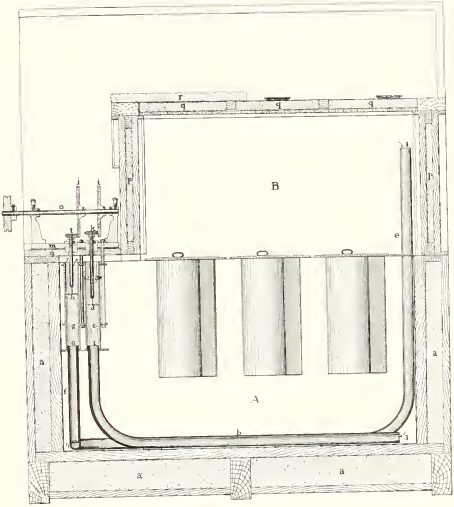

Fig. 1ª.

temperature is sufficient to make the determination of osmotic pressure very unsatisfactory. To overcome this difficulty a constant temperature bath has been devised by Morse and Frazer. A detailed description of the structure of the bath is published in the American Chemical Journal for July 1906, but a brief description will suffice for the present purpose.

The bath consists of a doube-walled wooden box, the interior of which is lined with copper. The space between the walls is packed with hair felt. The capacity of the tank is 335 liters, it being filled with distilled water. Above the tank and resting upon it, is another box of the same width as the tank but only about three-fourths as long. This air chamber may be opened at the top and front by means of hinged doors, the one in front being provided with a plate glass window through which the readings are made. When closed and an experiment is in progress the bath is made as nearly air tight as possible. Fig.1^a is a vertical section through the center of the bath, A being the tank and B the air chamber. The lead pipe b lies upon the bottom of the tank and by means of the propeller d water is drawn in at 3 and delivered near the surface of the water at 2. In this way the water is kept in circulation and an even temperature secured. Two

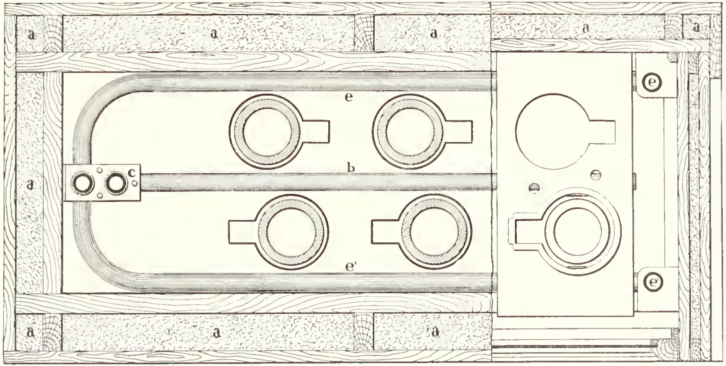

Fig 2.

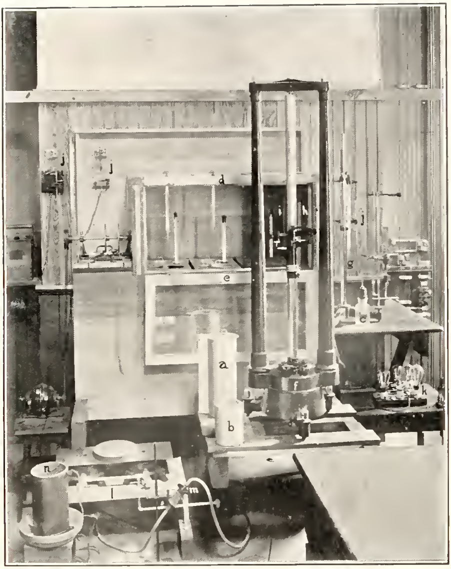

Fig 3.

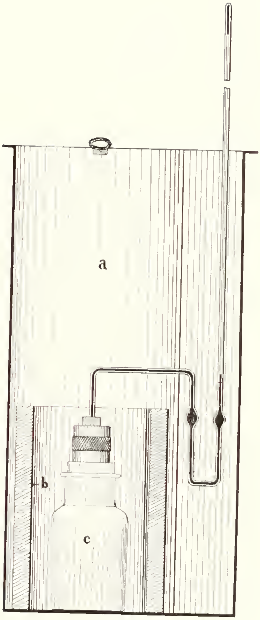

Fig. 4.

additional lead pipes, one of which is shown at E, in a similar manner conduct the air from 4 down through the water and deliver it at 7, thus keeping the air at nearly the same temperature as the water. The arrangementof the pipes b, e and e′, is also seen in Fig.2, which is a horizontal section of the bath. The machinery by which the propellers are driven is situated outside of the bath. It consists of the shaft O, Fig.1ᵃ, and the disks i and j which drive the pulleys k and l by friction. The resulting speed can be regulated as desired by varying the distance from the center at which the pulleys run. Just above the surface of the water are three iron plates one of which is shown in place at the right of Fig.2. These iron plates support galvanized iron cans, a Fig. 3, the arrangement of which is shown in Figs.1ᵃ and 2. The cans are weighted with heavy cast iron cylinders; b Fig.3, within which is placed the bottle, carrying the cell and manometer. The arrangement of the can, the cylinder and manometer is shown in Fig.4. The bath is provided with six thermometers, three for air and three for water; their distribution is seen in Fig.3. To protect the contents of the bath from changing temperatures on the outside, the top and sides are covered with pads of hair felt. The pad which covers the window in front is provided with slits so a reading may be made without exposing more than small part of the glass to outside temperatures.

In order to guard still farther against outside changes of temperature, the bath cathetometer and standard meter scale are covered by a tent made by stretching heavy muslin upon a wooden frame. This structure is double-walled, the sides being coated with sizing to make the cloth more nearly air tight. The ceiling is both sized and painted. The temperature within this enclosure is regulated by an electric stove, n Fig. 3, which is controlled by a thermostat. The room in which the enclosure is built has its own temperature regulated by a gas stove, shown at l. The supply of gas is controlled by the device m by which the gas is automatically turned on or off as the temperature of the room requires.

By means of these arrangements the temperature is controlled within narrow limits provided the temperature out of doors does not rise much above the highest temperature at which the thermostats are set. In the cooler season the usual daily variation in the outer room is less than 0°.6 and within the enclosure the range is generally less than 0°.25, while such slight temperature changes as occur within the bath itself are so gradual that their effect is negligible. The former difficulties occasioned by changes in temperature are therefore entirely avoided, except during the summer months.

TAKING DOWN A CELL.

After a cell has developed its maximum pressure and all necessary readings have been made, it is removed from the bottle m Fig.1, the pressure is gradually released by unscrewing the collar g and the stopper k is withdrawn with the aid of the "fang." The cell is rinsed and filled with distilled water and allowed to stand in distilled water till it is needed for another experiment when the deposition of the membrane must be repeated. Before the manometer can be used again it is necessary to remove the solution which is left in the lower end. If the new solution differs widely in concentration from that which was previously used, it is generally better to replace with mercury that portion of the solution which remains in the manometer and then replace a portion of the mercury with the new solution.. This operation presents some difficulty if the enlargement at j is a bulb as in the older forms of the manometer. If the pressure at j is diminished the air enclosed in the manometer expands driving out the solution, which is of course followed by the mercury. When the mercury reaches the top of the bulb j it forms drops which, on account of their greater specific gravity, fall through the solution in j and are lost, while the bulb itself remains filled with solution.

It is generally necessary in such cases to immerse the bulb in a suitable reservoir of mercury and then to increase the pressure by means of a bicycle pump. In this way, the solution, followed by the mercury from the reservoir, is driven over into the first large bulb of the manometer. If sufficient pressure is brought to bear on the mercury in the reservoir, drops of mercury may be made to fall across through the solution in the large bulb, so increasing the amount of mercury which will be left in the manometer at atmospheric pressure. Now, by gradually decreasing the pressure a part of the solution is driven out at the end of the manometer. It is evident that this method will not remove the solution from the bulb itself while the manometer is in an upright position. In order to remove the last portions of the solution the end of the manometer is immersed in a dish containing mercury, then a small tube which has been drawn out to a fine point and bent at two right angles is inserted in j so the open end is in the solution. Then when the solution is drawn out by suction, mercury takes its place. When the enlargement at j is made by thickening the walls of the tube without increasing its bore, no special difficulty is experienced in removing the solution which remains in the manometer after an experiment. The usual method in this case is to immerse the end of the manometer in mercury and

apply diminished pressure until all the solution has been driven out. When atmospheric pressure is restored mercury takes the place of the solution which has been removed. After the lower end of the manometer is filled with mercury, a quantity of the new solution is introduced by immersing the end of the manometer in the solution and applying diminished pressure, when drops of mercury are forced out of the end of the manometer. In this way it is possible to introduce as much of the new solution as desired.

When the new solution is of the same concentration as the old, or when there is only a small difference in their concentrations, the procedure is much simpler especially in the new form of the manometer. Under these circumstances, it is unnecessary to displace the old solution with mercury. The end of the manometer is immersed in the new solution and diminished pressure applied until the thread of mercury is drawn over just to the end of the manometer. After being held in this position for a time, atmospheric pressure is restored when a portion of the mixed solutions enters the manometer. After repeating this process several times with fresh portions of the new solution, the manometer is ready for use.

OSMOTIC BEHAVIOR OF UREA SOLUTIONS.

Attempts were made to measure the osmotic pressure of urea solutions, using a copper ferrocyanide membrane. The cell used was designated as No.00 and manometer No.9 was employed. The results of the various attempts are tabulated below:

Date	Resistance of membrane in ohms.	Solutions used	Pressure Developed in atmospheres.
Nov.30	90000		
Dec.1	120000		
" 8	120000	.5N urea	3
" 9	111000	.5N urea	2
" 11	111000	.5N urea	2
" 13	55000	.5N cane sugar	10.5
" 18	52000	.5N urea	4.3
" 21	30000		
" 22	40000		
" 23	42000	.5N urea	3.7
" 27	27000		
" 28	33000		
Jan.2	37000		
" 5	37000	.5N cane sugar	14.

Later attempts to secure satisfactory measurements of pressure with urea solutions were likewise unsuccessful, the pressure developing very slowly, there being no well defined maximum. These repeated failures cannot be attributed to the membrane or the cell wall since under the same conditions cane sugar solutions developed a much greater pressure which was, in both cases, maintained for 24 hours or longer. It is to be noted that, with a single exception, after each experiment in which a urea solution was used, the membrane failed to develope as great a resistance as

it showed before the experiment was tried. This would naturally suggest that the trouble might be in the action of the urea solution upon the membrane itself. Experiments were undertaken with an idea of showing whether or not urea would act upon copper ferrocyanide, but no action at atmospheric pressure could be detected. No attempts were made to study the action of urea under pressure. Another possible explanation which suggested itself is that the membrane used permits the urea solution to escape. But no urea could be detected in the solution in which the cell was immersed. A satisfactory explantion of the peculiar osmotic behavior of urea is lacking.

On account of the unsatisfactory behavior of urea solutions as regards osmotic pressure, it was thought that sufficient time was not available for a complete investigation of this substance. The manometers and cells were turned over to Mr. E.F. Lovelace who used them in the work of measuring the osmotic pressure of glucose solutions, and the investigation described in Part 11 was taken up.

OSMOTIC PRESSURE OF GLUCOSE SOLUTIONS.

In the study of the osmotic pressure of glucose solutions new difficulties were encountered.

It was found that some of the cells which are perfectly satisfactory in measuring the osmotic pressure of cane sugar solutions, cannot be used with glucose solutions for the reason that the membrane permits the escape of the dissolved substance. Only those cells are available which contain an especially good membrane. The fact that glucose escapes from the cell during an experiment is shown in two ways: First, it is to be noticed that in nearly every one of the following experiments the rotation of the cell contents after the completion of an experiment is less than the original rotation, and the difference in rotation is too great to be accounted for by the dilution of the solution within the cell; second, the presence of glucose in the water in which the cell is immersed, has been repeatedly shown by evaporation to dryness, charring and the odor of burnt sugar being easily observed. As a consequence of this leakage, the results in the first experiments were generally low, even after the application of a correction based upon the loss in rotation.

A much greater difficulty was soon encountered. Usually about four days were required for a cell to reach its maximum and after so long a time fermentation is to be expected, especially in solutions which are so fermentable as are those of glucose. Soon after

this series of experiments was begun it was noticed that the cells were covered with a mold, which proved to be the common Penicillium. The growth multiplied rapidly until the cells were practically useless for the measurement of pressure. It became evident that if successful measurements were to be made upon glucose solutions, some means must be devised for preventing or at least delaying fermentation. Investigations along this line are now in progress.

On account of these difficulties the measurements which were obtained on the osmotic pressure of glucose solutions must be considered merely preliminary. They are of value only in so far as they indicate the directions in which work is needed. The cells used in these measurements were known as C and D. These cells have been newly prepared, and their efficiency was first shown by testing with solutions of canesugar. They were not used for experiments with glucose until they were shown to be capable of developing the theoretical pressure to be expected from a cane sugar solution of any definite concentration.

In the following record of experiments, the rotation of the original solution and of the solution at the conclusion of an experiment was determined by means of a saccharimeter, care being taken to avoid error from birotation. The loss in rotation is

due chiefly to leakage, although the correction to be applied is practically the same as it would be if the loss in rotation was caused by dilution, since the escaped glucose is dissolved in such a large volume of water. The number of calibration units of air in the manometer at atmospheric pressure is determined from the data given in connection with the calibtation and determination of the air volume. In the first column is given the time at which the successive readings were made. Column 4 shows the final volume of air in the manometer at the temperature recorded in column 3, and column 5 shows the final volume of air reduced to 0°. By dividing this latter value into the original volume of air, the quotient obtained shows the pressure in atmospheres to which the air in the manometer is subjected. To obtain the osmotic pressure several corrections must be applied. The pressure of the atmosphere aids osmotic pressure hence it is necessary to substract atmospheric pressure from the pressure exerted upon the air column. On the other hand osmotic pressure is opposed by the pressure of the liquids in the manometer. The value of this correction is obtained from the height of the mercury and the height of the solution in the manometer. This correction must be added to the pressure exerted

upon the air column. There must also be added a correctionfor the depression of the meniscus in the capillary tube. When these corrections are all made, the result obtained is the osmotic pressure of the solution with which the cell is filled. But the concentration of this solution has been changed both by the water which has entered the cell and by the glucose which has escaped. The magnitude of this correction is determined from the loss in rotation which the solution has suffered during the experiment. By making this additional correction, the osmotic pressure is obtained for the concentration under investigation.

It will beobserved that no correction has been introduced for the displacement of the manometer while under pressure. In all these experiments the displacement was so slight that it could not be detected, so no correction of this sort is called for. In more accurate determinations a correction must also be introduced because of the shape of the meniscus while it is under pressure. This correction is important for the more concentrated solutions, but it was not introduced in these experiments because they are not of sufficient accuracy. The meniscus correction is umimportant in the case of dilute solutions.

In more accurate work the variations from Boyle's Law must also be considered in determining the true value of the osmotic pressure.

The theoretical gas pressure is the pressure which would be exerted by a molecular equivalent of hydrogen, if it is confined to the same volume as that occupied by the pure solvent. The values given are obtained from the formula.

$$G = 22.265\ (1 + .00367\ t)$$

in which G is the theoretical pressure exerted by the gas at the temperature t.

The molecular weights are calculated from the observed osmotic pressure are upon the H = 1 basis and are obtained from the formula-

$$M = \frac{W(22.265 + .0816\ t)}{P}$$

M being the desired molecular weights, W the weight of glucose used in 1000 grams of solvent, t the temperature of the solution and P the observed osmotic pressure.

The following are the results of the individual experiments:(1)

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(1) The author is indebted to Mr. E.F. Lovelace for these measurements.

SUBSTANCE Glucose

Original Wt. Normal Concentration of Solution .1 N	Experiment No. 1
Rotation of Original Solution [illegible]	Manometer Used No. 8
Rotation at Conclusion of Experiment 4°7	Capillary Depression [illegible]
Loss in Rotation 26%	Cell Used D
Calibration Units of Air in Manometer 70.76	Resistance of Membrane [illegible]
Time of Setting up Cell 5:00 PM Jan [illegible]	Initial Pressure

Time	Temperature		Volume of Air in Manometer		Corrections				Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Leakage ~~Inversion~~	Capillary Depression				
Jan. 24 9:00 PM	21.[illegible]	[illegible]	1[illegible]3.90	[illegible]	.01	[illegible]						
Jan 25 8:30 AM	21.7	22.6	[illegible]0.04	17.83	.01	0.47						
1.00 PM	21.8	22.6	1[illegible]6.58	[illegible]	.01	0.47						
5:20 PM	21.[illegible]	22.8	184.[illegible]	[illegible]	1.01	0.47						
[illegible]:00 PM	21.9	22.8	[illegible] 82	[illegible]	.01	0.47						
Jan 26 [illegible]:00 AM	22.0	22.8	[illegible] 23	10[illegible].2	.01	0.47						
[illegible] PM	22.1	22.8	[illegible]	[illegible]06.[illegible]	.01	0.47						
5:00 PM	22.1	22.9	1[illegible]9.80	[illegible]	.01	0.47						
Jan 27 [illegible]:00 AM	22.2	22.9	1[illegible]8	104.0[illegible]	1.00	0.47						
4 30 PM	22.3	23.0	1[illegible]81	63.[illegible]	.00	0.47	0.22	0.02	2.41	2.41	0.00	[illegible]
Jan 28 10:30 AM	22.[illegible]	23.1	1[illegible].73	63.8	0.9[illegible]	0.47	0.22	0.02	2.42	2.41	+0.01	178.[illegible]
6.00 PM	22.[illegible]	23.[illegible]	[illegible]7[illegible]	[illegible].8[illegible]	[illegible]	0.47	[illegible]	0.02	2.42	2.41	+0.01	[illegible]8.0

SUBSTANCE Glucose

Original Wt. Normal Concentration of Solution 1/n

Rotation of Original Solution [illegible]

Rotation at Conclusion of Experiment 0°.4

Loss in Rotation 0

Calibration Units of Air in Manometer [illegible].46

Time of Setting up Cell 2:00 PM Jan 2[illegible]

Experiment No. 2

Manometer Used No.

Capillary Depression .02 [illegible]

Cell Used C

Resistance of Membrane

Initial Pressure

Time	Temperature		Volume of Air in Manometer		Corrections				Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Inversion	Capillary Depression				
Jan 2[illegible] 7.00 PM	21.7	22.7	[illegible].36	174.72	[illegible]	0.40						
Jan 26 9.00 AM	22.0	22.8	[illegible]1.30	176.60	1.01	0.40						
2.00 PM	22.1	22.8	[illegible]	[illegible]	1.01	0.40						
5.10 PM	22.1	22.9	[illegible]	[illegible]	1.01	[illegible]						
Jan 27 [illegible]00	22.2	[illegible]	[illegible].66	[illegible]	1.00	[illegible]						
2.00 PM	22.3	23.0	184.10	169.31	1.00	0.41						
4.30 PM	22.3	23.1	184.04	169.67	1.00	0.41						
Jan 28 10.30 AM	22.4	23.1	183.42	67.12	0.99	0.41		0.02	[illegible]	[illegible]	- [illegible]	[illegible]
[illegible]00 PM	22.5	23.1	[illegible]	[illegible].10	[illegible]	0.41	—	0.02	[illegible]	2.41	- [illegible]	[illegible]
Jan 29 2.30 PM	22.6	23.1	[illegible].12	[illegible]	1.00	0.41	—	0.02	2.23	2.41	- [illegible]	[illegible]
4.30 PM	22.6	23.1	[illegible]	[illegible]	1.00	0.41	—	0.02	2.23	2.41	- [illegible]	[illegible]
Jan 30 10.00 AM	[illegible]	[illegible]	[illegible]	[illegible].81	[illegible]	0.41	—	0.02	2.23	[illegible]	[illegible]	[illegible]

SUBSTANCE Glucose

Original Wt. Normal Concentration of Solution .2 N

Rotation of Original Solution 16°

Rotation at Conclusion of Experiment [illegible]

Loss in Rotation 1.7°

Calibration Units of Air in Manometer 471.27

Time of Setting up Cell 4:30 PM Jan 30 190[illegible]

Experiment No. 3

Manometer Used No. 8

Capillary Depression [illegible]

Cell Used F

Resistance of Membrane [illegible]

Initial Pressure

Time	Temperature		Volume of Air in Manometer		Corrections				Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Leak ~~Inversion~~	Capillary Depression				
Jan 30 8:00 PM	22.0	22.3	102.61	97.22	.00	0.[illegible]	0.09	0.02	4.23			
Jan 31 8:30 am	22.1	22.5	1[illegible]2.73	94.7[illegible]	[illegible]	0.57						
2:00 PM	22.1	22.6	102.15	[illegible]	[illegible]	0.51						
4:10 PM	22.1	22.8	10[illegible]	97.88	1.00	0.[illegible]						
7:30 PM	22.1	22.9	101.35	93.45	1.00	0.[illegible]						
Feb. 1 [illegible]:00 am	22.3	22.8	102.18	92.3[illegible]	[illegible]	0.[illegible]						
[illegible]:00 PM	22.3	22.7	[illegible]0.04	9[illegible].30	0.99	0.58	0.09	0.02	4.49	4.82	-0.33	181.[illegible]
Feb. 2 11:[illegible] am	22.3	23.7	[illegible]	91.[illegible]	.01	0.58	0.09	0.02	4.03	4.32	-.29	190.2
4:30 PM	22.4	23.7	[illegible].31	91.11	[illegible]	0.58	0.09	0.02	4.04	4.32	-0.[illegible]	18[illegible]
Feb. 3 [illegible]:30 am	22.[illegible]	22.8	[illegible]	90.[illegible]	1.01	0.58	0.09	0.02	[illegible]	4.81	[illegible]	18[illegible]

SUBSTANCE [illegible]

Original Wt. Normal Concentration of Solution .2 N	Experiment No. 4
Rotation of Original Solution [illegible]	Manometer Used No. 1
Rotation at Conclusion of Experiment 0.3	Capillary Depression .02 millimeters
Loss in Rotation 2.8 %	Cell Used 3
Calibration Units of Air in Manometer 4.7.4.6	Resistance of Membrane 28 [illegible]
Time of Setting up Cell 3:30 PM Jan 31 1906	Initial Pressure

Time	Temperature		Volume of Air in Manometer		Corrections				Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Leakage ~~Inversion~~	Capillary Depression				
Jan 31 7:30 PM	22.1	22.4	13.51	04.[illegible]	1.00	0.31						
Feb 1 11:00 AM	22.3	22.8	108.90	00.91	1.00	0.31						
4:00 PM	22.3	22.4	108.40	100.07	1.00	0.31						
Feb 2 11.0 AM	22.3	23.7	06.0	97.60	1.00	0.31						
4:30 PM	22.4	23.1	100.[illegible]	[illegible]	1.00	0.31	0.13	0.02	4.48	4.8[illegible]	-0.37	
Feb 3 10:30 AM	22.4	22.8	07.61	96.[illegible]	1.01	0.31	0.13	0.02	4.51	[illegible]	-0.31	
3:45 PM	22.4	22.8	04.38	96.32	1.01	0.31	0.13	0.02	7.02	[illegible]	-0.33	
Feb 4 10:00 AM	22.3	21.6	103.04	[illegible].61	1.01	0.31	0.13	0.02	[illegible]	[illegible]	-0.2[illegible]	[illegible]
[illegible] PM	22.3	[illegible]	10[illegible]	[illegible]	1.01	0.31	0.13	0.02	4.[illegible]	4.8[illegible]	[illegible]	18[illegible].0

SUBSTANCE Glucose

Original Wt. Normal Concentration of Solution .3 N

Rotation of Original Solution 16.°0

Rotation at Conclusion of Experiment 15.°2

Loss in Rotation 0.°8

Calibration Units of Air in Manometer 441.97

Time of Setting up Cell 3:15 PM Feb 3, 1906

Experiment No. 6

Manometer Used No. 11

Capillary Depression .02 [illegible]

Cell Used D

Resistance of Membrane 81000 [illegible]

Initial Pressure

Time	Temperature		Volume of Air in Manometer		Corrections				Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Leakage ~~Inversion~~	Capillary Depression				
Feb 3 5:30 PM	22.3	22.3	70.84	[illegible]0.81	1.01	[illegible]		0.02				
Feb 4 10:00 AM	22.4	22.7	67.98	63.77	1.01	0.62		0.02				
4:15 PM	[illegible].3	22.8	68.67	63.40	1.01	0.62		0.02				
Feb 5 10.30 AM	22.3	22.8	68.03	62.77	1.01	0.62		0.02				
5:00 PM	22.3	22.7	67.87	62.62	1.01	0.62	0.22	0.02	6.[illegible]	723	- 0.33	18[illegible].0
Feb 6 10:00 AM	22.3	22.6	67.68	62.57	1.01	0.62	0.22	0.02	6.72	723	- 0.31	186.7
4:00 PM	22.3	22.5	67.72	62.[illegible]7	1.01	0.62	0.22	0.02	6.[illegible]	723	- 0.31	[illegible]6.1
Feb 7 11.00 AM	22.3	22.8	67.77	62.[illegible]	1.01	0.62	0.22	0.02	[illegible]	723	0.31	[illegible]

SUBSTANCE Glucose

Original Wt. Normal Concentration of Solution .3 N

Rotation of Original Solution 5°.5

Rotation at Conclusion of Experiment 5°.2

Loss in Rotation 3.25

Calibration Units of Air in Manometer 467.46

Time of Setting up Cell 4.00 PM Feb 6 1908

Experiment No. 6

Manometer Used No. 9

Capillary Depression .02 atmosphere

Cell Used C

Resistance of Membrane

Initial Pressure

TIME	TEMPERATURE		VOLUME OF AIR IN MANOMETER		CORRECTIONS				Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Leakage ~~Inversion~~	Capillary Depression				
Feb. 7 11:00 am	22.3	22.8	75.39	69.08	1.01	0.55		0.02				
6:00 PM	22.2	22.7	75.40	69.02	1.01	0.55		0.02				
Feb. 8 11:00 am	22.2	22.6	75.16	69.44	1.01	0.55		0.02				
6:00 PM	22.3	23.0	75.22	69.38	1.01	0.55		0.02				
Feb 9 11:00 am	22.1	21.8	74.44	68.94	1.00	0.56	0.2	0.02	6.60	7.22	− 0.62	195.7
4:30 PM	22.1	23.3	74.55	68.70	1.01	0.56	0.2	0.02	6.62	7.22	− 0.60	195.0
Feb 10 11:00 am	22.2	23.3	74.32	68.48	1.01	0.56	0.21	0.02	6.64	7.22	− 0.58	194.5

SUBSTANCE Glucose

Original Wt. Normal Concentration of Solution .4 N
Rotation of Original Solution 20°.8
Rotation at Conclusion of Experiment 20°.0
Loss in Rotation 3.8%
Calibration Units of Air in Manometer 441.97%
Time of Setting up Cell 4:30 PM Feb. 8 1906

Experiment No. 7
Manometer Used No. 8
Capillary Depression .02 atmosphere
Cell Used D
Resistance of Membrane
Initial Pressure

Time	Temperature		Volume of Air in Manometer		Corrections				Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Leakage ~~Inversion~~	Capillary Depression				
Feb. 9 11:00 am	22.2	21.8	56.50	52.31	1.00	0.64						
4:30 PM	22.1	23.3	56.95	52.39	.00	0.64						
Feb. 10 11:00 am	22.2	23.3	56.24	51.82	1.01	0.64						
3:30 PM	22.2	22.7	55.52	51.27	1.01	0.64						
Feb. 11 11:00 am	22.2	22.5	53.94	49.83	1.03	0.64	0.34	0.02	8.83	9.63	-0.80	195.1
5:30 PM	22.2	22.3	53.70	49.64	1.03	0.64	0.34	0.02	8.87	9.63	-0.76	194.2
Feb. 12 10:00 am	22.2	22.2	53.32	49.32	1.02	0.64	0.34	0.02	8.94	9.63	-0.69	192.6
4:00 PM	22.1	21.8	53.23	49.28	1.02	0.64	0.34	0.02	8.94	9.63	-0.69	192.7

SUBSTANCE Glucose

Original Wt. Normal Concentration of Solution .4 N

Rotation of Original Solution 20°.8

Rotation at Conclusion of Experiment 20°.3

Loss in Rotation 2.4%

Calibration Units of Air in Manometer 441.97

Time of Setting up Cell 4:00 PM Feb. 20 1906

Experiment No. 8

Manometer Used No. 8

Capillary Depression .02 atmosphere

Cell Used C

Resistance of Membrane 29,700 Ohms

Initial Pressure

Time	Temperature		Volume of Air in Manometer		Corrections				Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Leakage ~~Inversion~~	Capillary Depression				
Feb. 20 9:00 PM	22.1	23.2	59.09	54.47	1.00	0.64		0.02				
Feb. 21 9:00 am	22.3	23.5	53.85	49.58	1.00	0.64		0.02				
5:00 PM	22.4	23.6	52.89	48.68	.99	0.64		0.02				
Feb. 22 9:00 am	22.7	23.6	51.85	47.72	1.00	0.64		0.02				
7:00 PM	22.8	23.5	51.60	47.51	1.00	0.64	0.22	0.02	9.18	9.65	−0.47	180.0
Feb. 23 11:00 am	23.	23.6	51.91	47.78	1.00	0.64	0.22	0.02	9.13	9.66	−0.53	189.2
7.00 PM	23.1	23.8	52.11	47.93	1.00	0.64	0.22	0.02	9.10	9.66	−0.56	189.8
Feb 25 11:00 am	23.2	23.8	52.54	48.33	1.00	0.64	0.22	0.02	9.02	9.66	−0.64	191.6

The results shown in the foregoing experiments are tabulated, the values given being the mean of those found.

TABLE 1V

Experiment Number	Concentration	Observed Osmotic Pressure	Theoretical Gas Pressure
1	.1N	2.42	2.41
2	.1N	2.23	2.41
3	.2N	4.53	4.82
4	.2N	4.53	4.82
5	.3N	6.92	7.23
6	.3N	6.62	7.22
7	.4N	8.90	9.63
8	.4N	9.11	9.66

TABLE lV continued

Difference	Calculated Molecular Weight	Theoretical Molecular Weight	Difference
0.01	178.63	178.74	-00.11
-0.18	193.76	178.74	15.02
-0.29	190.43	178.74	11.69
-0.29	188.70	178.74	9.96
-0.31	186.77	178.74	8.03
-0.60	195.10	178.74	16.36
-0.73	193.65	178.74	14.91
-0.55	187.50	178.74	8.76
Mean	189.31	178.74	10.54

The results as shown are far from satisfactory but they indicate some of the problems to be solved in measuring the osmotic pressure of glucose solutions. The results are, however, sufficiently accurate to justify the prediction that glucose solutions, when made up upon the weight normal basis, will obey the gas law so far as their osmotic pressure is concerned.

PART 11

FREEZING POINT AND DENSITY.(1)

A. Glucose Solutions.

FREEZING POINT APPARATUS

The apparatus used in determining the freezing point lowerings is a modification of the usual apparatus.(2) The testtube which holds the solution whose freezing point is to be determined is 275 mm. long and about 26 mm. internal diameter. This is placed in a larger glass tube 275 mm. long and 44 mm. in diameter. The freezing mixture is held in a galvanized iron cylinder 305 mm. long and 117 mm. in diameter. The cylinder is covered with hair felt and is provided with a cover which has an opening to receive the glass tubes and one for the admission of the freezing mixture.

The thermometer used is one especially made for this work. The scale is 245 mm. long and it records temperatures from + 1° to - 5°, being graduated to hundredths of a degree.

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(1) The author is indebted to Mr. P.B. Dunbar for assistance in this work.

(2) Jones, Freezing POint, Boiling Point and Conductivity Methods.

Temperatures are read directly. The stem from the top of the bulb to the bottom of the scale is 180 mm. long. The thermometer is known as PTR 23997 and has been compared with the standard gas thermometer at the Physikalisch - Technische Reichsanstalt. A table of certified corrections accompanies the instrument, which states that the zero point is at +0°.2 on the scale, but the most careful tests in the laboratory show the zero point to be at +0°.4. It is probable that this change in the zero point has been caused by a slight contraction in the bulb. This would cause a similar displacement of all the corrections which should be applied to the thermometer readings. Accordingly it was assumed that correspondingly greater corrections must be applied at the points indicated by the certificate. These corrections apply on the condition that the thermometer is immersed up to the bottom of the scale in the solution whose temperature is to be determined and the remainer of the instrument is kept at a mean temperature of 20°. It is impossible to realize these conditions exactly in a freezing point apparatus and attempts to approximate these conditions were not successful, so it became necessary to find other conditions which would give satisfactory

results. It was found that if the thermometer is immersed in solution to a certain mark on its stem and placed in position in a freezing mixture which has a temperature of about -5°, the zero point is the same as when the thermometer is surrounded by its standard conditions. These modified conditions were used in all freezing point determinations, the observed readings being corrected by means of a curve. When in position for a determination the thermometer is held in place by a strong cork which is always placed at the same point on the stem. The cork is provided with three openings- for the thermometer, the stirrer and for the admission of ice. On account of its long stem, it is importanct that the thermometer be held firmly in the center of the tube in order to avoid coming in contact with the stirrer or the wall of the tube.

MATERIAL.

The glucose used was obtained from Kahlbaum. According to Richter if the crystals contain a molecule of water they should melt at 86° and lose water at 110°, but if they are anhydrous, they will melt at 146°, Tests made upon the material used show it to have a fairly sharp melting point at 146°, without any visable change at lower temperatures.

Two analyses(1) show the following results:

	1	11	Theoretical for anhydrous Glucose	Theorectial hydrated glucose
C	39.85	39.73	39.98	36.34
H	6.81	6.77	6.71	7.12

Accordingly the glucose is considered anhydrous and very nearly pure. The material was finely pulverized and dried over calcium chloride.

The water used was ordinary distilled water, a supply being kept in a bottle near the balance case. The freezing point of the pure solvent was determined whenever it became necessary to refill the bottle and at frequent intervals during the work.

METHOD.

All solutions are made weight normal - a gram molecular weight, on the H = 1 basis, is dissolved in 1000 g of water, proper corrections being applied for displacement of air. The method of preparing solutions is as follows: A clear and dry weighing bottle and stopper are weighed, then filled with glucose and weighed again; the amount of water necessary to make a solution of the desired concentration from this amount of material is calculated and exactly this amount of water is weighed into an Erlenmeyer flask which has been fitted

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(1) Made by C.W. Gray.

with a glass ground stopper; then the glucose and the containing bottle are added to the water in the flask. By this method the glucose is exposed to the air only when it is being transferred from a dessicator to the weighing bottle. There is also very little loss of the solvent by evaporation. At least two solutions of each concentration were made each solution being designated by a number such as 1,11, 111 &c.

In carrying out a determination the solution is cooled to the zero point before it is poured into the test tube, in order to avoid unnecessary exposure to the air. The inner test tube with the thermometer and stirrer in position is first placed directly in a freezing mixture which contains a large amount of salt. In this way the solution is cooled rapidly to a point about one degree below the temperature at which it is suspected the solution will freeze. When this point is reached the test tube is quickly transferred to its outer jacket which is surrounded by a freezing mixture, the temperature of which is kept from five to seven degrees below the freezing point of the solution. The temperature of the latter mixture is controlled approximately by adding a weighed amount of salt, it being found that 25 - 35 grams of ordinary fine salt would give

a temperature of from - .5° to - 9°. It is necessary in every case to test the temperature with a small thermometer since the manner in which the salt is distributed through the ice will influence the resulting temperature materially. The thermometer is read through a reading glass, thousandths of a degree being estimated. In order to avoid any error from parallax a piece of paper having an opening about 6 mm. in diameter is pasted on the lens and the readings are made through the center of the opening. In order that the eye of the observer may at each reading be in the same position with respect to the top of the mercury column in the thermometer, the readings are made with the marks on the scale forming straight lines across the field. If the eye is too high or too low these lines appear curved.

RESULTS

The results of each determination are shown in the table below. Column 1V contains the corrected readings of the thermometer when ice begins to separate; Column V shows the highest reading, corrected, after ice begins to separate, the readings in this column being numerically equal to the freezing point lowering uncorrected for the separation of ice;

Column V

FOLD OUT

FOLD OUT

DENSITY.

The densities were determined by means of two pyknometers, designated as L and LL which were especially made(1) for this work. The side tubes were made from fine capillary tubing, a bulb being blown near the rear end in order to provide for the expansion of the enclosed liquid. In order to decrease the danger of loss through the bulb a slight upward bend is given the tube just in front of the bulb. To prevent loss by evaporation through the capillary side tubes, caps were made from glass tubing and these are slipped over the ends of the pyknometers after they are filled to the mark. Unless otherwise stated in the individual experiments the pyknometers were filled at zero. Portions of the solutions made for freezing point determinations were used, and,since the densities could be determined with much greater accuracy than the freezing points, the former was regarded as a check upon the accuracy with which a solution was made up. Owing to the ease with which glucose solutions ferment it was necessary to use only freshly prepared solutions. Several attempts were made to use solutions which had been kept over night in glass stoppered bottles

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(1) By B.F. Lovelace.

which were packed in ice. In each case bubles of gas appeared in the pyknometer as soon as it reached room temperature, the more concentrated solutions apparently fermenting most easily.

The capacity of the pyknometers was determined at frequent intervals during the work. In the capacity determinations the pyknometers are filled with the pure solvent and treated in the same manner as when they are filled with a solution. The method used for calculation is best explained by an example. Seven determinations of the weight of water held by L gave the following results:

	17.6025
	17.6025
	17.6026
	17.6030
	17.6026
	17.6022
	17.6025
Mean	17.6026

The weight of air displaced is determined from the formula(1)

$$W = P + Pa\ (\frac{1}{d} - \frac{1}{d'})$$

and in this case is found to be .0209. Then the weight of the water in vacuo is 17.6235. The value(2) .999874 is used as the density of water at zero. 17.6235 ÷ .999874 = 17.6257 which is the weight of water at 4° which is required to fill the pyknometer at 0°. Since the density of water at 4°

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(1) Morse Exercises in Quantitative Chemistry p24.
(2) From Landolt and Börnstein.

is unity 17.6257 is also the capacity of the pyknometer in cubic centimeters.

METHOD.

The solution whose density is to be determined is cooled to the zero point before it is removed from the flask in which it was made up. Then a portion sufficient to fill the pyknometer is poured into a cold dry evaparating dish and the pyknometer is filled as quickly as possible in the usual way by suction. Care is taken not to allow the solution to advance more than centimeter beyond the mark. The tip of the pyknometer which was dipped into the solution is carefully cleaned and the pyknometer is immersed in a zero bath of ice and water, which is provided with a strong stirrer. After remaining in this position for 15 minutes it is filled to the mark and if there is no change in the position of the meniscus after 5 minutes, the pyknometer is placed in a bath whose temperature is two or three degrees higher than that of the room. The advantages in placing the pyknometer in this bath are (1) the solutions expand more quickly (2) the glass is more easily dried when it is slightly warm and (3) there is less danger of moisture condensing from the air. With glucose solutions

it is important not to use too warm a bath on account of the ease with which fermentation begins at slightly elevated temperatures. After the solution has expanded the pyknometer is removed, carefully dried on a soft linen cloth and placed by the side of the balance case. After the temperature has become uniform the weighing is made. All weighings are made by substitution, proper corrections being made for air displacement.

DENSITY AT THE FREEZING POINT.

In most of the determinations of the density of glucose solutions the pyknometers were filled at zero. It was desired to determine corresponding values when the pyknometers are filled at the freezing point. The normal solution was chosen as the one which would be most likely to show the greatest difference between the density at zero and the density at its freezing point. In order to fill the pyknometer at the desired temperature a freezing point apparatus, similar to the one previously described, was used. The inner tube was large enough to admit the pyknometer and a stirrer. This tube is filled with a solution of cane sugar which is so prepared that its freezing point

is the same as that of solution whose density is to be determined. In the preparation of this low temperature bath reference was made to the work of Morse and Frazer(1) and from the data given by them the amount of sugar necessary to give a solution which would freeze at -1°.92 was calculated by interpolation. After the solution was prepared its freezing point, determined in the usual way, was found to be -1°.93. The pyknometer was immersed in a bath of this sugar solution and the thermometer inserted to the bottom of its scale. After the bath had been cooled below zero and before the freezing point was reached a piece of dry ice was dropped in to prevent undercooling. It was found impossible to control the temperature closer than one tenth of a degree, but the difference in density over such a small range is more than equaled by the average error in weighing. Parallel determinations were made, one pyknometer being filled at zero and the other at the freezing point of normal glucose solution. The following are the results obtained:

	Density at Zero	Density at Freezing Point	Difference
1	1.06309	1.06319	.00010
11	1.06292	1.06304	.00012

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(1) Am. Chem. Jour. 34 95

These differences are regarded as so little greater than the experimental error that the work was not carried to more dilute solutions where the differences would be still less. The determinations given on the first line above were made upon a fresh solution while those on the second line were made after the same solution had been kept over night packed in ice. It will be observed that the density of the solution had changed by an amount which is greater than the difference between the density at zero and that at the freezing point.

RESULTS.

The zero densities obtained in the individual experiments are shown below:

TABLE V1

Date	Concentration	Solution Number	Pyknometer	Density
3/2	$\frac{N}{10}$	1	L	1.00687
3/3	$\frac{N}{10}$	1	L	1.00687
3/3	$\frac{N}{10}$	11	L	1.00687
3/5	$\frac{N}{10}$	111	L	1.00687
		Mean		1.00687
3/8	.2N	1	L	1.01373
3/9	.2N	1	L	1.01371
3/9	.2N	1	L	1.01377
3/9	.2N	1	L	1.01378
4/6	.2N	11	LL	1.01380
4/6	.2N	11	L	1.01377
		Mean		1.01376
3/10	.3N	1	L	1.02041
3/10	.3N	1	L	1.02041
3/31	.3N	11	I	1.02038
3/31	.3N	11	LL	1.02045
		Mean		1.02041

TABLE V1 (continued)

Date	Concentration	Solution Number	Pyknometer	Density
3/13	.4N	1	L	1.02691
3/14	.4N	11	L	1.02691
3/14	.4N	11	L	1.02691
3/15	.4N	111	L	1.02691
3/15	.4N	111	L	1.02691
		Mean		1.02691
3/16	.5N	1	L	1.03331
3/17	.5N	1	LL	1.03319
3/19	.5N	11	L	1.03331
3/19	.5N	11	LL	1.03329
		Mean		1.03327
3/19	.6N	1	L	1.03946
3/19	.6N	1	L	1.03945
3/19	.6N	1	LL	1.03945
3/20	.6N	11	L	1.03946
3/20	.6N	11	LL	1.03944
		Mean		1.03945

TABLE V1 (continued)

Date	Concentration	Solution Number	Pyknometer	Density
3/21	.7N	1	L	1.04554
3/21	.7N	1	LL	1.04548
3/22	.7N	11	L	1.04544
3/22	.7N	11	LL	1.04563
3/22	.7N	11	LL	1.04548
		Mean		1.04551
3/23	.8N	1	L	1.05136
3/23	.8N	1	LL	1.05138
3/24	.8N	11	L	1.05152
3/24	.8N	11	LL	1.05154
		Mean		1.05145
3/26	.9N	1	L	1.05729
3/26	.9N	1	LL	1.05703
3/26	.9N	11	L	1.05736
3/30	.9N	111	LL	1.05735
4/7	.9N	1V	L	1.05739
4/7	.9N	1V	LL	1.05741
		Mean		1.05731

TABLE V1 (continued)

Date	Concentration	Solution Number	Pyknometer	Density
3/29	N	1	L	1.06298
3/29	N	1	LL	1.06293
4/2	N	111	LL	1.06302
4/4	N	111	LL	1.06292
4/4	N	111	L	1.06304
5/11	N	1V	L	1.06305
5/11	N	1V	LL	1.06305
		Mean		1.06300

The following table gives a summary of the densities and freezing point lowerings of glucose solutions. Column 11 is the mean of the determinations for each concentration; Column 111 is the difference between the densities of two successive concentrations; Column 1V is the volume of the solution taking the volume of the pure solvent as unity; V shows the difference in successive readings in 1V; column V1 is the mean of the observed lowerings of the freezing points; V11 is the difference between successive readings in V1; V111 shows the multiples of the lowering observed for $\frac{N}{10}$ solution; 1X contains the differences between the observed lowering and the values given in V111; X1 is the freezing point lowering as calculated by the formula $\Delta = 1.85$ ND; and X11 shows the differences between the values in X1 and the corresponding observed lowerings shown in V1.

FOLD OUT

ıces

6

1

0

2

4

7

16

28

40

48

A study of this table shows that when glucose solutions are made up on the weight normal basis their properties are very closely, if not exactly, a function of the amount of dissolved substance. Thus the densities increase with concentration by an amount which is quite uniform, and the molecular lowering is a constant. It is to be noticed also that the observed lowerings are in each case very nearly equal to the multiples of the lowering observed for $\frac{N}{10}$ solutions. The close parallel between the observed lowerings and that calculated by the formula $\Delta = 1.85$ N.D. is likewise worthy of attention.

It is a well known fact that when glucose is crystallized from aqueous solutions at ordinary temperatures, it carries with it a molecule of water of crystallization. If each molecule of the anhydrous glucose, when dissolved in water, removes from the solvent one molecule of water, then each solution in table 111 is more concentrated than appears from the amount of water used in making up the solution. In the normal solution, which contains a gram molecular weight of glucose in 1000 grams of water, this concentration, due to hydration, would amount

to the removal of a gram molecule of water. Accordingly there would remain 982 grams of water which would act as solvent and the solution would be 1.018 normal. Applying the same reasoning to the other concentrations where the amount of water extracted is proportionately less because the amount of glucose present is less, the concentration of the solutions is easily obtained. From these values and the observed lowerings of the freezing point the molecular lowerings are obtained in the usual way. The results of such computation are shown in the table below, the corresponding values, obtained on the supposition that glucose in solution is not hydrated, being given for comparison.

Table V111

Concentration of hydrated glucose	Molecular Lowering of hydrated glucose	Molecular Lowering if glucose is not hydrated	Differences
.100+	1.92	1.92	.00
.201	1.92	1.92	.00
.301	1.91	1.92	.01
.403	1.89	1.91	.02
.505	1.89	1.91	.02
.607	1.89	1.91	.02
.709	1.89	1.91	.02
.812	1.88	1.91	.03
.915	1.88	1.91	.03
1.018	1.88	1.92	.04

If we assume that each molecule of glucose takes up a molecule of water from the solvent

then the molecular lowering is not a constant but becomes a continually decreasing quantity as the concentration increases. But if dilute solutions of non-dissociated substances obey the gas law then the molecular lowering will be a constant. These considerations indictate that while glucose may come out of an aqueous solution with a molecule of water of crystallization, it has no power of withdrawing that molecule from the solvent in which it is dissolved.

B. CANE SUGAR SOLUTIONS.

FREEZING POINT

The freezing point lowerings of cane sugar solutions were determined in the same manner as for the glucose solutions. The sugar was obtained by pulverizing rock candy. The water used in this work was prepared according to the method used in the preparation of water for conductivity measurements.

The following table shows the results obtained:

FOLD OUT

FOLD OUT

FOLD OUT

FOLD OUT

DENSITY AT THE FREEZING POINT

When the densities are to be determined at zero, the procedure is precisely the same as that described under glucose solutions. But it was desired to determine the density also at the freezing point and at the temperature of maximum density. The efforts to determine the density of a normal glucose solution at its freezing point show that with ordinary appliances it is impossible to maintain for any length of time a definite temperature below zero. Even when a pyknometer is immersed in a bath whose freezing point is the same as that of the solution in the pyknometer, the temperature will vary within narrow limits. When this bath is a sugar solution of known freezing point several difficulties arise: (1) the bath must be exposed to the air so its own freezing point varies constantly because of the evaporation of the solvent; (2) a new bath has to be carefully prepared for each concentration whose density is to be determined; (3) inversion and fermentation make it impossible to keep the bath for any length of time. These difficulties are avoided by using as a low

temperature bath a solution of common salt, the freezing point of which is lower than the lowest temperature at which the pyknometer is to be filled. This solution is placed in a test tube which is capable of holding about 350 C.C. and is large enough to receive the pyknometer, thermometer and a stirrer. This tube is surrounded by an air jacket and this in turn is packed in a freezing mixture of salt and ice. The apparatus used is essentially an enlarged form of the freezing point apparatus. The large volume of the salt bath, aided by the surrounding air jacket, causes the temperature of the bath to fall very slowly- on an average of about 6 or 7 degrees per hour. It is assumed that on account of this gradual change of temperature the solution in the pyknometer is always at the temperature indicated by the thermometer. This assumption seems to be justified by the fact that perfectly concordant results are obtained in this way. When the temperature at which the density of the solution is to be determined is reached, the pyknometer is filled to the mark and treated in the same manner as previously described. The thermometer used in this work is one which

has been tested at the Reichsantalt, it being known as P.T.R 26260. The scale which is 255 mm. in length is from -35° to + 50°. It is graduated to fifths of a degree.

DENSITY AT THE TEMPERATURE OF MAXIMUM DENSITY.

The temperature of maximum density of the sugar solutions is determined by using the same salt bath. As the solution in the pyknometer is cooled down, the meniscus in the fine capillary side tube is observed to move up to a certain point and then return. When the temperature changes slowly it is possible to fill the pyknometer while the meniscus is at its highest point. With the apparatus used there is usually a range of from 0°4 to 0°6 over which no motion of the meniscus is noticable. As a consequence two readings are made and the mean is taken as the temperature of maximum density. When the pyknometer is filled with a concentrated solution some difficulty is experienced in making the reading below the temperature of maximum density, because the meniscus does not move out as rapidly as in the case of the more dilute solutions. In consequence the temperature

of maximum density as recorded in table V is less reliable for concentrations greater than .6 normal. This uncertainty does not materially affect the accuracy of the density at the temperature of maximum density since the method employed does not require this temperature to be known except for the sake of computing the capacity of the pyknometer.

In making a determination the pyknometer is filled to a point beyond the mark and a piece of coordinate paper is placed beneath the capillary tube. The motion of meniscus can be watched very closely in this way. The pyknometer is filled to the mark when it becomes evident that the meniscus will advance no farther. The pyknometer is allowed to remain in the bath until the temperature has fallen still lower and the meniscus begins to retreat. After it becomes evident that the solution in the pyknometer is below the temperature of maximum density, the inner tube and its air jacket are removed from the freezing mixture and are exposed to the temperature of the room. The changes in temperature under these conditions take place more slowly and uniformly than when the bath is being cooled down in the freezing mixture, presumably

because the surrounding air is itself of a more uniform temperature than is the freezing mixture. As the pyknometer warms up the meniscus again advances and at its highest point should stadd just tangent to the mark.

When this method was first put into practice some doubt was felt as to its accuracy. To test the method a determination was made upon the purest water obtainable. In this experiment no change in the position of the meniscus could be observed between +4° and +4°.4. According to custom + 4°.2 is considered the temperature of maximum density as determined by this method. The actual temperature of maximum density of water as recorded by various observers in Landolt and Börnstein is from 3°.74 to 4°.7. The density of water determined at the temperature of maximum density was found to be 1.000009. Considering that the water used was not absolutely pure, these results show that the method is sufficiently accurate for the present purpose.

In computing the density of any solution at its freezing point or at the temperature of maximum density it is of course necessary to calculate the capacity of the pyknometer at the temperature in question. This calculation is made from the

formula -

$$C_t = \frac{C_o}{1 + .000026\ t}$$

In which C_t is the capacity at any temperature, t, below zero and C_o is the capacity at zero. If the temperature t is above zero then the expression becomes -

$$C_t \equiv \frac{C_o}{1 - .000026\ t}$$

The results of the individual experiments are given in the following table:

TABLE X

Date	Concentration	Solution Number	Pyknometer	Temperature	Density
4/12	.1N	1	L	0°	1.01310
	.1N	1	L	0°	1.01309
4/17	.1N	11	LL	0°	1.01308
	.1N	11	L	-0°.2	1.01310
4/18	.1N	11	L	+4°.2	1.01303
4/22	.1N	111	L	+4°.2	1.01312
	.1N	111	LL	0°	1.01309
4/21	.2N	1	L	+3°.2	1.02575
	.2N	1	LL	0°	1.02575
4/22	.2N	11	L	+3°.2	1.02568
	.2N	11	L	+3°.2	1.02563
	.2N	11	LL	0°	1.02573
4/24	.3N	1	L	+1°	1.03786
	.3N	1	LL	0°	1.03786
	.3N	1	L	0°	1.03788
	.3N	1	LL	0°	1.03788
4/25	.3N	11	L	+1°	1.03787
4/26	.4N	1	L	0°	1.04952
	.4N	1	LL	0°	1.04951
	.4N	11	L	-0°.4	1.04953
	.4N	11	LL	0°	1.04951
4/27	.5N	1	L	-1°.9	1.06078
	.5N	1	L	-1°.9	1.06079
	.5N	1	LL	0°	1.06068
	.5N	1	LL	0°	1.06068
4/28	.5N	11	L	0°	1.06067
	.5N	11	LL	0°	1.06066
5/1	.6N	1	LL	0°	1.07136
	.6N	1	L	-3°.7	1.07160
	.6N	11	L	-3°.7	1.07159
	.6N	11	LL	0°	1.07137
	.6N	11	L	-1°.2	1.07139
5/2	.6N	111	L	0°	1.07135

TABLE X (continued)

Date	Concentration	Solution Number	Pyknometer	Temperature	Density
5/3	.7N	1	L	-5°.	1.08202
	.7N	1	LL	0°	1.08168
	.7N	1	LL	0°	1.08169
	.7N	11	LL	0°	1.08164
	.7N	11	L	-1°.4	1.08180
	.7N	11	L	-5°	1.08206
5/4	.8N	1	LL	0°	1.09156
	.8N	1	LL	0°	1.09155
	.8N	1	L	-6°	1.09204
5/7	.8N	11	L	-6°	1.09203
	.8N	11	LL	0°	1.09156
	.8N	11	L	-1°.6	1.09163
5/8	.9N	1	L	-7°.5	1.10175
	.9N	1	LL	0°	1.10107
5/9	.9N	11	LL	0°	1.10107
	.9N	11	L	-1°.8	1.10116
4/10	N	1	L	0°	1.11021
	N	1	L	-2°.1	1.11057
4/11	N	11	LL	0°	1.11027
	N	11	LL	0°	1.11027
	N	11	L	-2°.1	1.11054

In order that the densities found may be more readily compared the mean values are given -

TABLE X1

	Zero	Freezing Point		Temperature of Maximum Density	
	Density	T_f	Density	T_m	Density
.1N	1.01309	-0°.2	1.01310	+4°.2	1.01310
.2N	1.02574	-0°.4		+3°.2	1.02570
.3N	1.03787	-0°.6		+1°.0	1.03787
.4N	1.04951	-0°.8		-0°.4	1.04953
.5N	1.06067	-1°.0		-1°.9	1.06079
.6N	1.07136	-1°.2	1.07139	-3°.7	1.07160
.7N	1.08167	-1°.4	1.08180	-5°.0	1.08204
.8N	1.09156	-1°.6	1.09167	-6°.0	1.09204
.9N	1.10107	-1°.8	1.10116	-7°.5	1.10175
N	1.11025	-2°.1	1.11056		1.11114

In tables X and X1 the temperatures given for the freezing points are rounded out to the nearest tenth, on account of the difficulty in filling the pyknometer at any definite temperature below zero. The densities at the freezing points were not determined for every concentration because in the more dilute solutions the freezing point lies so close to either zero or the temperature of maximum density that the difference in density is slightly, if any, in excess of the experimental error. It is to be noted that for solutions moreconcentrated than .4 normal the temperature of maximum density is below the freezing point. Such solutions, when undisturbed, freeze at

the bottom first. The undercooling necessary to make a maximum density determination in the .9 normal solution is at least 6 degrees. On account of the danger of breaking the pyknometer, the maximum density of the normal solution was not determined but its approximate value is obtained by extrapolation.

Table X11 gives a summary of the results obtained for cane sugar solutions. The densities used are those at the temperature of maximum density. The values given in each column are obtained in the same way as explained for table V11.

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The densities in this table show about the same relative increase with concentration as those found for glucose. From the data given in Column 1V it is evident that a solution containing 1000 grams of water and a gram molecular weight of sugar will occupy a volumn of 1205.61 cubic centimeters. Columns V1 V111 and 1X show that for solutions of cane sugar up to the .6 normal each concentration is a multiple of the .1 normal, but beyond this point abnormally great lowerings begin to appear. The molecular lowering also shows abnormalities beyond the .6 normal. In comparing the observed lowerings with those calculated from the formula $\Delta = 1.85$ N.D. it is evident that this formula holds more uniformly in cane sugar than in glucose.

BIOGRAPHY.

B. Smith Hopkins was born September 1,1873 at Owosso, Michigan. His early education was obtained from the public schools of that place. He entered Albion College in the fall of 1892 and graduated with the A.B. degree in 1896. The following year was spent in graduate work at the same institution, for which the degree of A.M. was received. Six years were spent in public school work and one in graduate work at Columbia University, New York. In October 1904 he entered the chemical department of Johns Hopkins University. His subordinate subjects are Physical Chemistry and Physics.